

Supplementary information

Fischer-Tropsch synthesis on ruthenium catalyst in two-phase systems: an excellent opportunity for the control of reaction rate and selectivity

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Preparation of catalysts

The powdered ruthenium on carbon (Ru/C) catalyst with 5 wt. % Ru was prepared by incipient wetness impregnation of hydrophobic carbon by aqueous solution of RuCl₃. The catalyst was dried at 100 °C and reduced in H₂ atmosphere at 500 °C during 3 h. The catalyst was cooled down till r.t. in H₂ atmosphere and flushed by He flow prior to withdrawal.

Characterization

The TEM analysis were carried out on a Jeol 2100F (field emission gun) microscope operating at 200 kV equipped with probe corrector for the spherical aberrations.

The amount of reversibly adsorbed carbon monoxide molecules on the catalyst surface was determined by SSITKA. The SSITKA apparatus is composed of two independent feed lines. The first line is dedicated to unlabeled compounds and tracer (CO, H₂, He and Ne), the second one to the isotopic compounds (¹³CO). Pressure transducers are used to adjust the same pressure drop for both lines. Isotopic switches were realized using a two-position four ways Valco-valve and monitored with f QMG 432 Omnistara in the Faraday mode. The catalyst (50 mg) was placed in the tubular millimetric fixed-bed reactor with plug-flow hydrodynamics and heated till 300 °C in the flow of He. For catalytic test, a total flow of 8.5 sccm/min was used with following composition 4He:1CO:2H₂:0.5Ne. SSITKA experiments were performed at atmospheric pressure and 300 °C.

Catalytic tests

Experiments were carried out in a 100 ml stirred autoclave operating in a batch mode and equipped with valve for sampling of gas phase. The procedure for testing catalysts in the reaction of CO hydrogenation was as follows: water and/or dodecane, catalyst Ru/C (0.3 g) and hexanol-1 in the case of experiment with surfactant was poured into the autoclave. The autoclave was purged and filled with CO (12.5 bar) and hydrogen (25 bar), the temperature was

increased to 220 °C and thereafter the catalytic experiment was started. Periodically gas samples were taken from the autoclave. Gaseous reaction products were analyzed online by gas chromatography. Analysis of H₂, CO, CO₂ and CH₄ was performed using Alltech CTR I column and a thermal conductivity detector. Hydrocarbons in the range C₁-C₇ were analysed using a capillary CP ParaBond Q with FID detector. The long chain hydrocarbon (C₁₃-C₆₀) were analysed by gas chromatography using a SimDist column with addition of dodecane as internal standard. Analysis of the hydrocarbon during FTS in the aqueous phase was conducted after extraction of hydrocarbons by addition of dodecane after reaction. Light products (till C₁₁) in organic phase (dodecane) were analyzed by GC (Varian) using a capillary CP PoraBond Q column.

Conversions of CO (mol %) and product selectivity (mol %) in hydrogenation experiments were defined as follows:

$$\text{Conversion (mol \%)} = (\text{moles of CO reacted})/(\text{moles of initial CO}) \cdot 100$$

$$\text{Selectivity (mol \%)} = (\text{moles of C atoms of product produced})/(\text{moles of CO reacted}) \cdot 100.$$

TEM

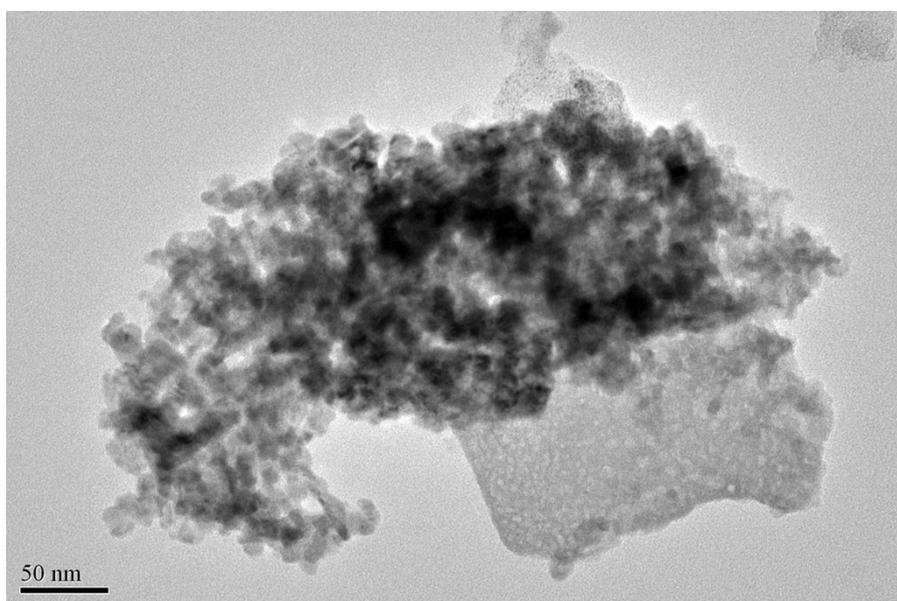


Fig. 1S. TEM image of the catalyst Ru/C

SSITKA

The amount of reversibly adsorbed carbon monoxide molecules on the catalyst surface was investigated using SSITKA with switches from ¹²CO/H₂/He/Ne to ¹³CO/H₂/He. A delay is

observed between response of inert tracer Ne (τ_{Ne}) and ^{12}CO (τ_{CO}) (Fig. S2). The delay indicates the presence of reversibly adsorbed carbon monoxide molecules on the catalyst surface which are in equilibrium under the reaction conditions with carbon monoxide in gaseous phase. The amount of carbon monoxide adsorption sites under the reaction conditions (Fig. S2) was estimated from the flow rate of carbon monoxide and transient delay ($\tau_{\text{CO}} - \tau_{\text{Ne}}$) which represents the average carbon monoxide residence time on the catalyst surface. The amount of adsorbed CO was $130 \mu\text{mol/g}$ of the catalyst. Thus, taking into account the amount of Ru on the catalyst ($450 \mu\text{mol/g}$) the dispersion of the metal is about 28 %.

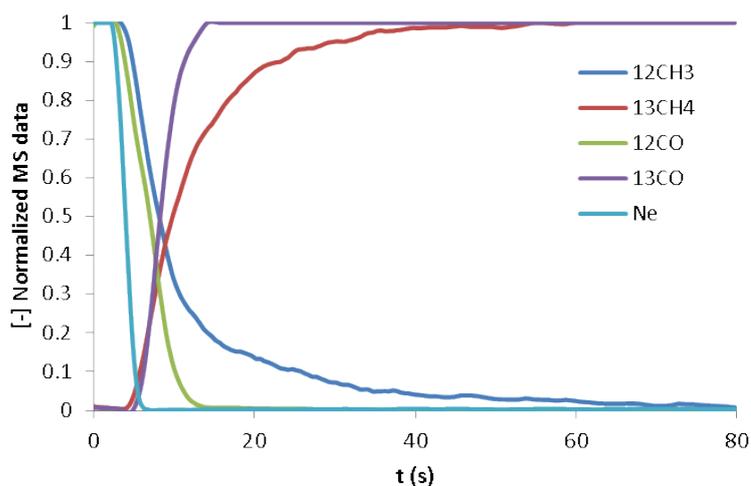


Fig. 2S. TEM image of the catalyst Ru/C

Selectivity to methane and CO_2

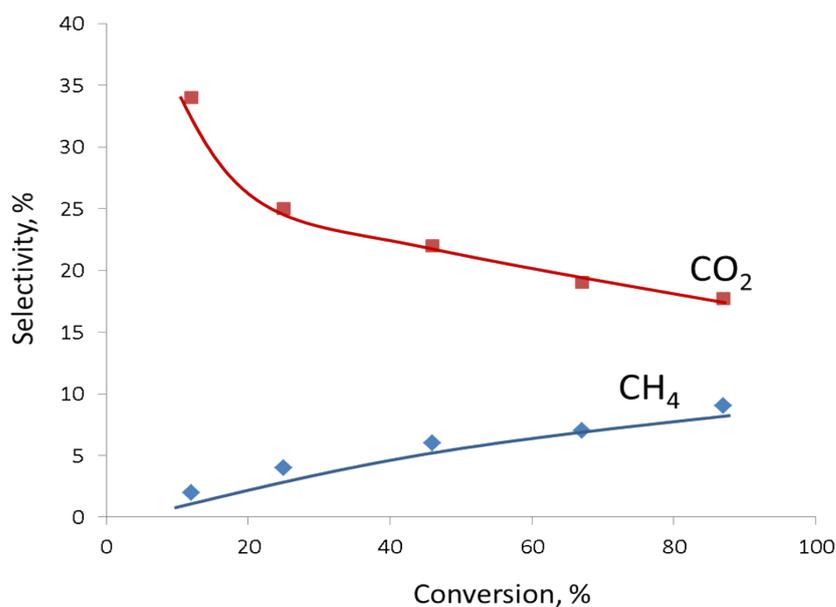


Fig. 3S. Selectivity to CH_4 and CO_2 depending on CO conversion during FTS in the aqueous phase (run 1)

Hydrocarbons distribution

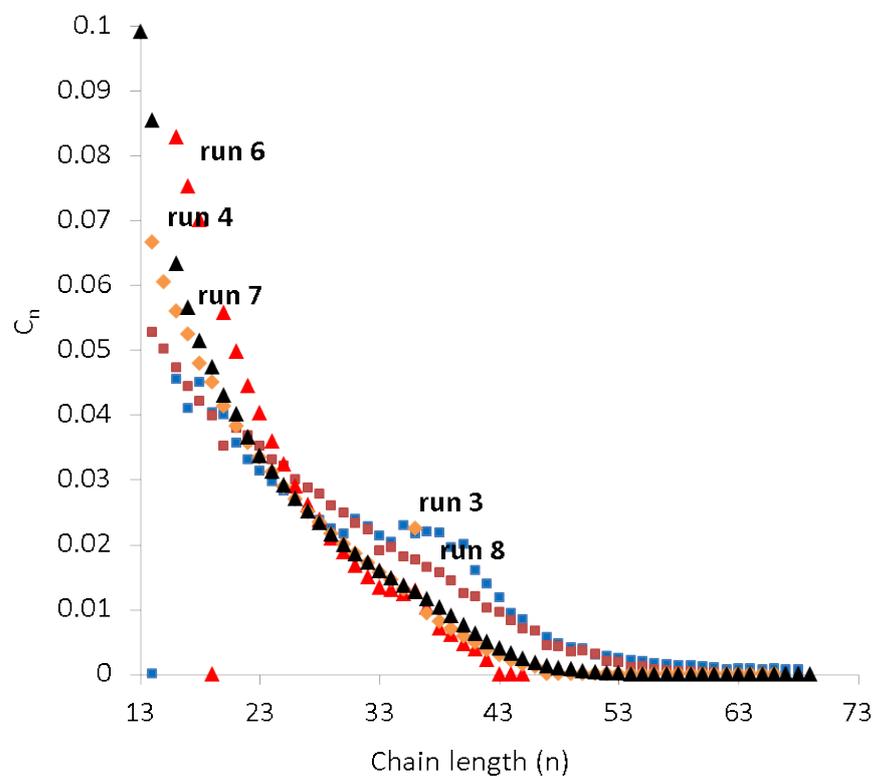


Fig. 4S. Distribution of hydrocarbons depending on the chain length.